

Fast-Curing Epoxy and Acrylate Adhesive Development for Adverse Marine Conditions

**by Daniel M. De Bonis, Steven Klankowski, Daniel Stewart, Ryan Robinson,
and John J. La Scala**

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Fast-Curing Epoxy and Acrylate Adhesive Development for Adverse Marine Conditions

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14. ABSTRACT Research efforts were made to develop a fast-curing underwater bonding adhesive. Commercial off-the-shelf adhesives were tested but found to lack both sufficient bond strength and cure speed when used for underwater applications. Several adhesives specifically formulated for underwater applications were also tested. These adhesives provided some improvement in bond strength but had very long cure times due to the water-tolerant curing mechanisms involved. It was determined that a new formulation of adhesive was needed to meet the goals of a fast curing adhesive for marine applications. The U.S. Army Research Laboratory experimented with formulating its own hybrid adhesives and curing agents specifically for underwater applications. This report focuses on the efforts to make two variations of a high-speed, high-strength underwater adhesive. One adhesive is a fast-curing epoxy modified with an acrylate monomer and the other a slower cure but stronger bonding acrylate adhesive. Experimentation also included solvent modifications and use of highly reactive acrylate monomers to promote underwater bonding.					
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1. Introduction

The U.S. Military utilizes adhesives for many applications including mechanical and structural bonding, repairs, and fabrication. Military operations often require adhesives to cure quickly and provide high performance unaffected by water or near-freezing temperatures.

Humidity and direct contact with water represents the greatest problems in terms of environmental stability for many adhesive joints. Water is a problem because its high polarity allows it to permeate most polymers used in adhesives. This can degrade the properties of the bulk adhesive or sealant itself, reduce the adhesion properties at the interface, and cause dimensional changes to certain adherents (1). Contact with water can significantly affect the bulk properties of the adhesive. Water contact can reduce the glass transition temperature, induce cracks, or initiate hydrolysis in which the water reacts chemically with the polymer. Hydrolysis causes the molecular bonds of the adhesive to break leading to decreases in strength and cohesive bond failures (1).

Commercial “waterproof” bonding adhesives are slow to cure and have relatively low bond strengths compared to adhesives formulated for dry applications (2). Adhesives fall short for use in adverse conditions for a variety of reasons. In two-component adhesive systems, the chemically reactive components needed for curing generally react poorly in the presence of water and create poor quality bonds. Tacky adhesives known as tackifiers are used to make tapes and double-sided applicator pads. These materials generally are limited in their application geometry and do not necessarily remain tacky when in contact with water. Light curable adhesives generally are less negatively affected by water but require external energy sources that make them less desirable from a logistical standpoint. Light radiation curable adhesives generally have lower adhesion, and the light does not penetrate the adhesives to great depths (3), limiting their use for thin bond lines only. Thermally cured adhesives use ambient thermal energy to induce polymerization, and the exothermic heat of reaction produced during polymerization accelerates and sustains the reaction, which proceeds via a variety of mechanisms (4). Few thermally cured adhesives result in rapid, high-strength adhesion, and even fewer function in high-moisture environments. Moisture reduces adhesion and the very high specific heat of water and potentially low water temperatures reduces exothermic cure acceleration for underwater adhesives. As a result, underwater adhesives either cure poorly or require long cure times of a day or more to obtain sufficient adhesive properties (4).

Ultra-fast-curing adhesive cyanoacrylates “Super Glues” such as 3M CA-40 anionically polymerize in the presence of moisture. In ambient environments with ~50% humidity, cyanoacrylates can fully cure within minutes (4). These types of adhesives can be used on a wide variety of substrates but are not recommended for use in wet environments (5). In wet

environments, the cyanoacrylates dissolve into the water immediately polymerizing and form no useful adhesive bonds.

Certain epoxy resin systems, such as National Maintenance Products NMP 3730, are formulated to set within minutes and reach near-complete cure within a few hours even underwater (6). However, it reaches full cure in hours, which is too slow for many Department of Defense applications.

The U.S. Army's current fast-curing battle damage repair adhesives Belzona 2311 elastomer, Belzona 1221 super metal, and Belzona metal plug all cure rapidly but fail to bond well in wet applications (7). Belzona 2311 is a fast-curing polyurethane adhesive. Belzona 1221 and metal plug are epoxy-amine polymers with an added isocyanate component, which quickly reacts with amines and generates heat to speed up the epoxy-amine reaction.

The U.S. Army Research Laboratory (ARL) achieved success in formulation of two adhesives for rapid underwater applications. Key to this technology was the selection of adhesive monomers and curing agents that minimally reacted with the water and the inclusion of solvents into the formulation. The solvents chosen decreased the cure time and provided a hydrophobic barrier to promote adhesive bonding.

2. Experimental Procedure

2.1 Materials

2.1.1 Commercially Available Adhesives

- 3M Scotch-Weld DP-805 Acrylic Adhesive: acrylic adhesive with fast cure and a high peel strength. Chemical structure: methyl methacrylate; synthetic polymer; 3,5-diethyl-1,2-dihydro-1-phenyl-2-propylpyridine; methacrylic acid.
- Devcon 1-min Epoxy: ultra-fast-setting epoxy that makes tough, durable bonds. Chemical structure: bisphenol-A diglycidyl ether resin and polyamide.
- Devcon 5-min Epoxy: rapid curing, general purpose adhesive that forms rigid bond. Chemical structure: Bisphenol-A diglycidyl ether resin and polyamide.
- Devcon Metal Welder: good adhesive qualities with steel and aluminum. Chemical structure: acrylate-based adhesive.
- Devcon Plastic Welder: similar strength and material quality in bonding but forms more slowly for better adhesion. Chemical structure: methacrylate-based adhesives.

- Devcon “Fastmetal” Metal Putty: high-performance alumina-filled epoxy for making fast emergency repairs. Chemical structure: epoxy resin/epoxy hardener.
- Loctite Metal Magic Steel Putty: versatile single-component iron filled epoxy repair putty. Chemical structure: epichlorohydrin-4,4'-isopropylidene diphenol resin, polyether polythiol, phenol, 2,4,6-tris[(dimethylamino)methyl].
- Lord 403 Acrylic Adhesive: chosen for its versatility in bond to a variety of substrates with minimal prep needed. Chemical structure: methacrylate based.

2.1.2 Lap Shear Samples

Prefabricated 2024 T3 aluminum lap specimen plates were utilized for single lap shear testing. Each plate contained five specimens. The plates had alignment guide holes which fit into a pegged base plate and provided a 12.7 ± 0.3 mm overlap. The specimens were designed to meet the requirements of ASTM standard D 3165-95 (8) to include ASTM B 209 “Specifications for Aluminum and Aluminum Alloy Sheet and Plate.”

Fiberglass composite test specimens were cut in the same dimensions as the aluminum specimens except for having a 1/4-in thickness. The fiberglass composite was cut from 2- × 2-ft scrap SC-15 epoxy/S1 fiberglass weave panels.

2.1.3 Acrylate Modifier Monomer

M Cure 400: chosen for its extremely fast cure rates, even at cold temperatures. Chemical structure: pentaerythritol tetraacrylate esters; pentaerythritol triacrylate esters; 1,6-hexanediol diacrylate.

2.1.4 Solvents

Nitromethane, chloroform, tetrahydrofuran, carbon tetrachloride, dichloromethane, acetone, benzene, toluene, N,N-dimethylaniline, methyl ethyl ketone, ethyl ether.

2.2 Cure Rate Testing

Specific event times were noted that included: working time, fixture time, functional cure, and full cure. The start time ($t = 0$) for calculating the events was when the adhesive was fully mixed. Working time is the period of time available to apply the adhesive and orient the item. Working time was from $t = 0$ until the adhesive began exhibiting reduced wetting of substrate upon application. Fixture time was represented by the time period in which the user could disengage from holding the repair item and it would remain in place. Fixture time was measured from $t = 0$ until the adhesive held the mixing stick firmly to the adhesive mass. Functional cure was measured from the start time of $t = 0$ until the adhesive bond was functional to the user. The item was considered to have reached its maximum adhesive bond after full cure had been reached. This was measured from $t = 0$ until the adhesive reached its maximum hardness based on indentation with a ball-point pen.

Adhesives were mixed in small disposable plastic mixing pans to establish basic curing characteristics. Commercial adhesives were prepared as recommended by the manufactures specifications. Approximately 10 g of each adhesive mixture was tested at 20 °C. Adhesives that cured too slowly were deselected from future testing.

2.3 Water Dispersion Solvent Testing

Prior experimentation noted high bond strengths in acrylate adhesives with high solvent content (9, 10). It was noted that these adhesives repelled water from the surface of wet aluminum when applied. Solvents identified in the formulations of the more successful underwater bonding adhesives were included in testing. Hydrophobic solvents were tested to determine their ability to repel water from the adhesive bonding area and in order to improve adhesion. An initial water dispersion test was conducted using a clean, grit-blasted 2024 T3 aluminum plate that was presoaked in DI-water on which individual uniform drops of solvent were placed and the radius of dispersion of the solvent was recorded

2.4 Water Uptake Testing

Test specimens were created using the finalized 1-min modified epoxy adhesive poured and cured into rectangular bars in silicone molds. These bars were then allowed to fully cure over the weekend and removed from their molds. The bars were weighed and placed in de-ionized or saltwater. Saltwater was made by adding sea salt to de-ionized water to achieve 3.5 weight-percent salinity. The bars were periodically removed, padded dry with a paper towel and weights recorded. Percent water uptake was calculated and recorded (equation 1). The modified 3M DP-805 was not tested as it did not have similar water uptake issues when left under water for long term.

$$\% \text{ Uptake} = \left(\frac{\text{Current Weight} - \text{Original Weight}}{\text{Original Weight}} \right) \times 100 \quad (1)$$

2.5 Viscosity Measurements

Viscosity measurements were conducted using a rehometer to determine the change in viscosity and shear stress as a function of shear rate. This was done to determine if the modified /unmodified version of 1-min epoxy and modified DP-805 retained useful shelf lives. It was found during experimentation that some modifications lead to increased cure speeds but ultimately lead to unacceptable reduction of shelf life. In order to be applied rapidly, adhesives needed to retain the ability to flow through a mixing nozzle. Experiments were done over a 3-month period at 25 °C, which was considered the minimum acceptable shelf life for special use military applications. Ideally, shelf life would be on the order of 1–2 years at room temperature.

2.6 Substrate Preparation

All-aluminum specimen plates were abrasive blasted using 180-grit aluminum oxide powder to clean off the area to be bonded. Blasting was sufficient to assure all surfaces used for adhesive contact were fully cleaned to remove any existing oxide layer. After blasting, specimen plates were triple rinsed with distilled water and allowed to air dry.

Painted aluminum test specimens were the same as above except they were painted with gloss black enamel paint and allowed to dry 24 h prior to application of any adhesives.

Fiberglass test specimens only used the smooth side of the panel for testing. The surface was roughened with 180-grit sand, cleaned with distilled water and dried prior to adhesive application.

2.7 Timed Strength Testing

Rapid Cure Testing Procedure. In order for adhesives to be considered useful, they had to be able to withstand a 14-kg/cm^2 (200-psi) instantaneous maximum load in under 2 min after application. A rapid-cure testing apparatus was constructed to adequately test these fast-curing adhesives to determine their cure strengths as a function of time (figure 1).

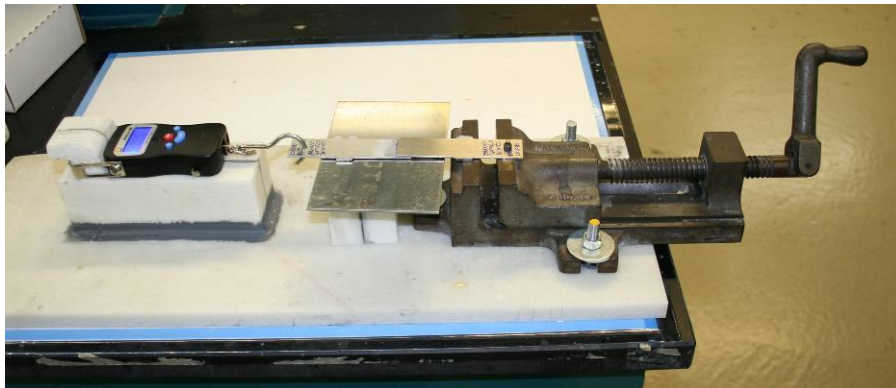


Figure 1. Rapid-cure testing fixture consisting of inline mounted digital scale and mounted drill press vise. Scale mount, moveable specimen support, and base were made from a high-strength/stiffness composite.

Lap specimens used were cut to ASTM standard D 3165-95 specification out of 2024 T3 aluminum. The aluminum met ASTM B 209 “Specifications for Aluminum and Aluminum Alloy Sheet and Plate.” Shear specimens were $4 \times 1 \times 1/16$ in with a 4-mm hole drilled into the non-prepped (non-sandblasted) end for attachment purposes. One specimen was attached to the apparatus via the scale hook and the other specimen was attached to the vice end via a threaded machine screw. Adhesive was applied to a single prepared lap shear specimen and the bond area was maintained at 12.7 ± 0.3 mm. A support table and removable spacers held the specimen pieces in line during the cure process. A 200-g weight was placed across the bond area

to assure sufficient contact during bonding. At the determined cure duration, the weight and spacers were removed. A hand crank was turned and tension was rapidly created to determine the maximum load. The maximum load was the highest registered reading, which held for at least 1 s. Cure duration was increased until the goal load reached 14 kg/cm^2 (200 psi) or 10 min was exceeded.

Previous experimental results shown in figure 2 indicated the most rapid cure was achievable with a two-part epoxy system. The fastest epoxy cure was achieved with the Devcon 1-min epoxy while the fastest acrylate bond was the 3M DP805.

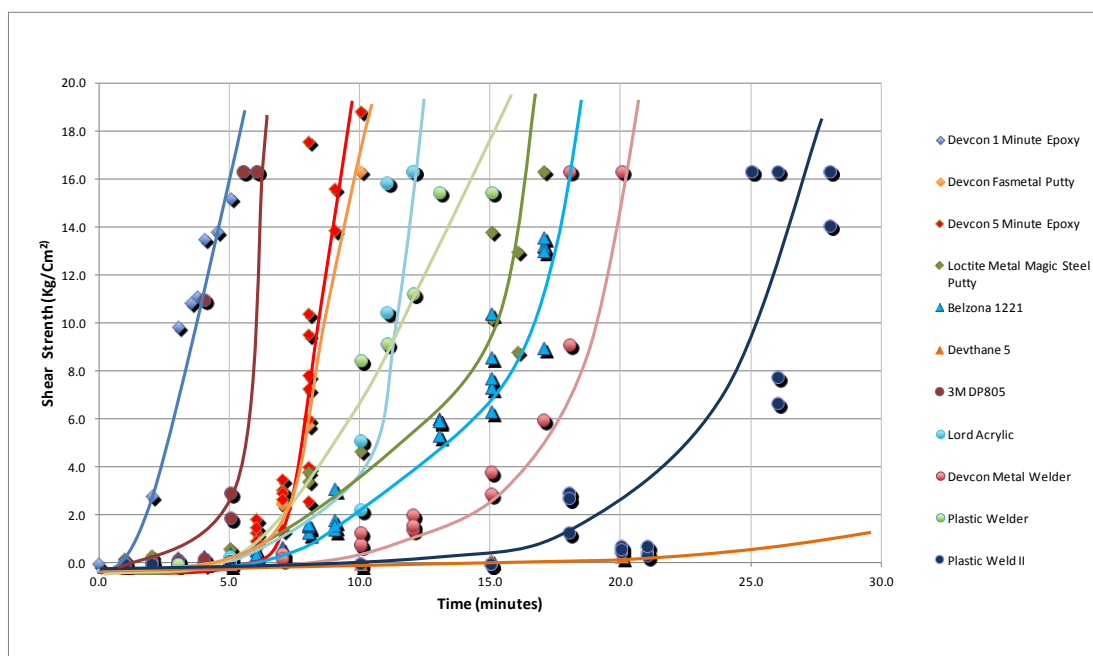


Figure 2. Lap shear load testing showing relative dry bond strength development over time (9).

In determining the strength of a bond that cured underwater, another test apparatus was constructed to allow an adhesive specimen to cure underwater in a fixed position and accurately load test each lap shear specimen (figure 3) based on the previous dry testing apparatus and lap shear specimens. One side of the specimen was fixed in place under water while the other side was hooked onto the scale. The two sections were then aligned underwater for a 1/2-in overlap. The specimen fixed to the scale was brought above water, adhesive applied, and then attached to the fixed submerged specimen. A rubber band was used to hold the two specimens together until the allotted testing period had passed. Once the rubber band was removed the apparatus worked in the same fashion as the dry testing version. The handle was cranked at a uniform speed and the scale monitored to determine the highest reading value.

Prior experimental results indicated the fastest underwater cures were achieved with the Devcon 1-min epoxy and the 3M DP805 acrylate adhesives (figure 4). The underwater data was comparative to the dry test data in figure 2.

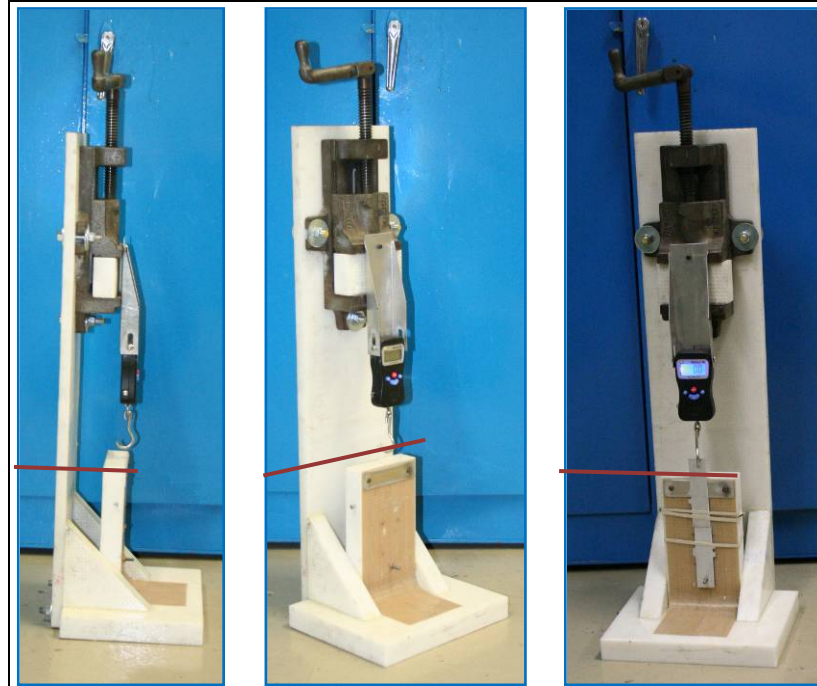


Figure 3. Photos of underwater testing apparatus. Red line indicates water line when submerged.

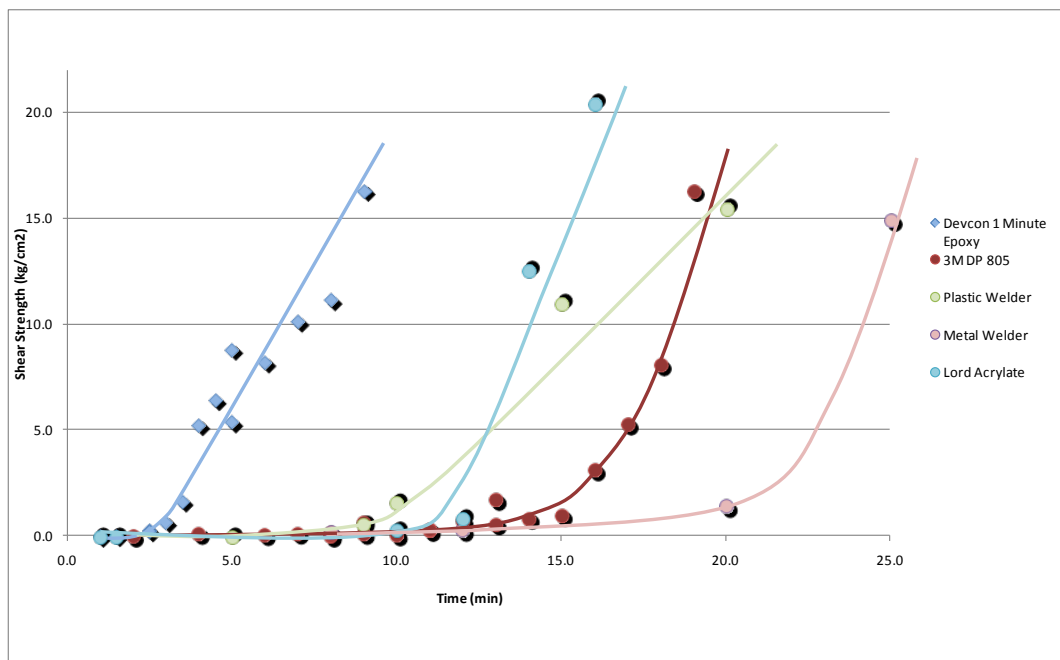


Figure 4. Previously tested commercial available adhesives tested for cure rate vs. bond strength underwater (10).

2.8 Mechanical Testing

2.8.1 Lap Shear Testing

Aluminum and fiberglass specimens were aligned in accordance with ASTM D 3165-95 “Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading of Single-Lap-Joint Laminated Assemblies” (8). The specimens had a 12.7 ± 0.3 -mm overlap between prepared adhesive test surfaces (figure 5).

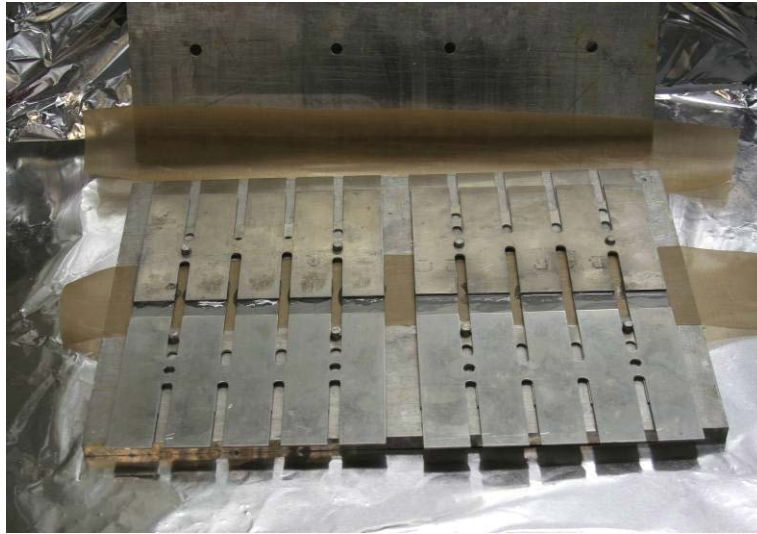


Figure 5. Dry lap shear plate setup prior to placement of alignment cover panel.

2.8.2 Dry Application Methodology

Once prepared, two lap specimen plates were placed on the pegged aluminum alignment panel. 20 g of adhesive were mixed on a small mixing tray with a wooden paddle. Once mixed, a new paddle was used to apply the adhesive onto the designated 12.7-mm overlap areas. If required, adhesive was applied using applicator guns with attached mixing nozzles. The corresponding prepared top cover panel was subsequently overlapped and pegged into place. Dummy plates were used to maintain proper spacing and release film was used to prevent adhesive from sticking to the alignment panels. The weight of the top alignment panel was sufficient to provide direct contact between lap specimens and the adhesive applied.

2.8.3 Wet Application Methodology

The alignment equipment setup used for the dry application methodology was also used for the wet application methodology. The aluminum alignment panels and specimen plates were kept under 7 cm of 21 °C tap water for 5 min prior to adhesive application. The top half of the lap specimen plates were removed from the water and were held vertically for 3 s and shaken once

prior to adhesive application. Immediately after application the lap plate was placed back into the water and adhered to the submerged corresponding bottom specimen plate. The top alignment panel was applied and samples were cured underwater for 12 h. Release fabric was used to prevent adhesion to alignment panels.

Once formulations were finalized, the adhesives (epoxy and acrylate) were put into 1:1 volumetric ratio cartridges. Disposable mix nozzles were required due to the rapid cure speeds and need for fast directed application underwater. This allowed for objects to be bonded entirely underwater. This application technique matched realistic underwater application under field conditions. This application technique was used for all finalized formulation bond speed and strength testing.

2.8.4 Instron Testing

Lap plates were cut into individual lap specimens and marked accordingly, as shown in figure 6.



Figure 6. Lap shear specimen cut into single specimen for mechanical lap shear testing.

Samples were tested following ASTM designation D 3165-95 (10). Load cells were selected according to ASTM recommendation to assure the maximum load fell between 15% and 85% of the load cell capacity. Cross-head loading speed was set to 1.27 mm/min. Recorded information included failure load, bond line thickness, type of failure, and bond area.

Experimentation conducted previously yielded the results found in figure 7. This data was valuable in selecting adhesives to modify.

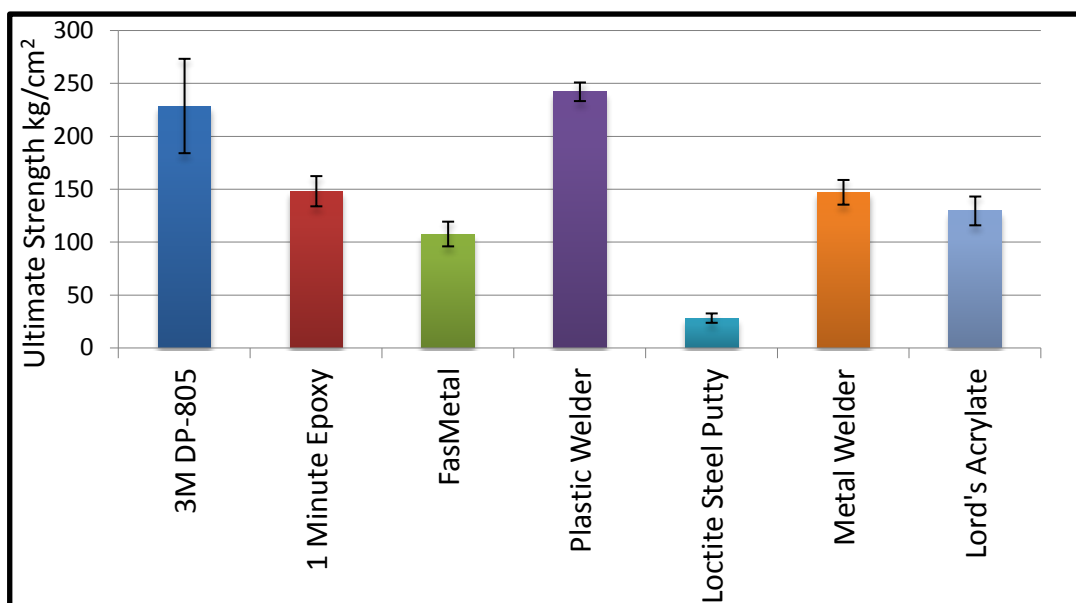


Figure 7. Ultimate dry lap shear strength for previously tested adhesives (10).

2.9 Formulation Selection

Based on the previous cure speed and ultimate lap shear results it was decided that two formulations of advanced fast curing adhesive would be formulated. One formulation would be an epoxy-based system. This system would be the fastest curing system but would likely be moderate in wet bond strength. For a stronger wet bond, it was decided to formulate a second acrylate-based adhesive.

The epoxy-based system chosen for modification and reformulation was the Devcon 1 min epoxy. It was a two-part epoxy that contained a useful color change indicator. When mixed, the blue color would disappear when fully mixed. This was especially useful as with such a rapid cure rate, it was important to know when the material was fully mixed so it could be applied as quickly as possible. Typically, one had to apply the mixed adhesive within a few seconds to achieve full bond strength. The color change was particularly noticeable later when using mixing nozzles.

The acrylate adhesive chosen for modification and reformulation was 3M DP805. It was the fastest curing acrylate and strongest underwater bonding adhesive tested. It still required a substantially long cure time of around 10–15 min to obtain 14-kg/cm² (200-psi) target bond strength.

2.10 Application Experiments

Experiments were conducted on the finalized modified 1-min epoxy adhesive formulation to collect data to construct a user's manual. This data included the working time, fixture time, functional cure, and full cure times. All application of adhesive was done entirely under water

using a manual cartridge and mixing nozzle application gun. Only the 1-min epoxy had significant enough increase in underwater cure speed to require a modified application technique. The end diameter of the mixing nozzle needed to be increase from 2 to 5 mm to accommodate the speed in which the adhesive needed to flow through the nozzle to prevent adhesive curing in the nozzle.

Application testing was conducted at three different water temperature levels. A large rectangular plastic tub was filled with warm water. A large, ¼-in-thick, 2- × 3-ft aluminum panel and steel attachment block were placed under the water line. If required, the water was chilled with ice to reach the desired temperature. The water temperature was tested with a digital thermometer to verify it had reached the target temperature for at least 3 min. Temperatures tested at were 0, 20, and 30 °C.

Working time was considered the time in which once the adhesive was applied to the substrate surface the operator had to position the applied object. Fixture time was reached when a 500-g steel block adhered to an aluminum panel remained in place when the panel was raised vertically up and out of its water bath and shaken. Functional cure was reached when the steel block could not be separated from the aluminum panel by holding the block only and shaking the panel. Full cure was the time in which the block and plate could not be separated by manual efforts. Parts fully cured required a hammer blow to separate.

3. Results and Discussion

3.1 Shear Strength

M Cure 400 acrylate monomer was added to both the 1-min epoxy and DP-805 adhesives. It was found that the ultimate shear strength decreases slightly as the amount of M Cure 400 was increased, as shown in figures 8 and 9. The decrease in strength was less severe with the acrylate-based DP805.

An epoxy step polymerization system (figure 10) is more sensitive to variation in the ratio of monomer and cure agent than in an acrylate system. The additional monomer added to the epoxy system would have resulted in the amine curing agent reacting with the M Cure 400 instead of an epoxy molecule. This would lead to an unbalance epoxy: amine ratio that would result in a decrease in shear strength.

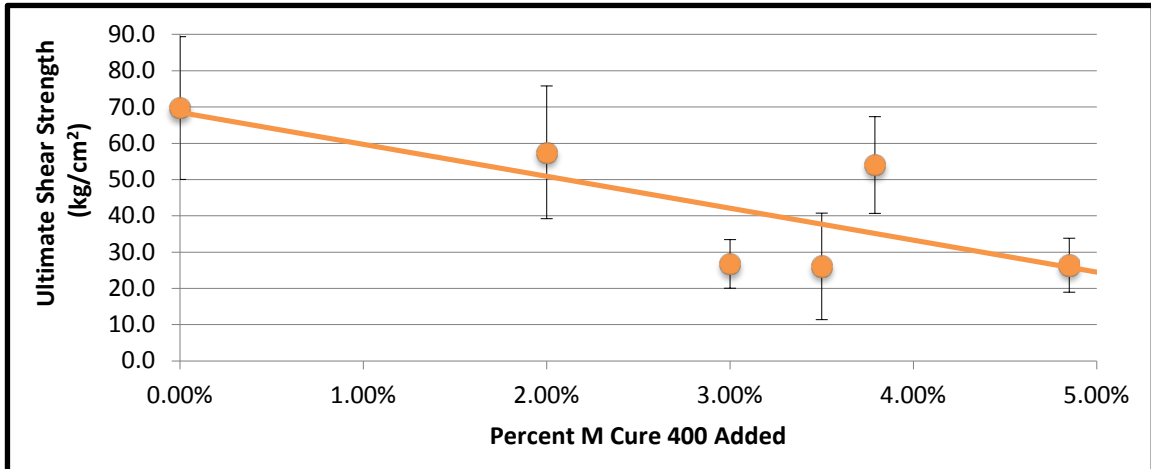


Figure 8. Averaged ultimate shear strength of 1-min epoxy modified with 2%–4.8% M Cure 400 (wet condition).

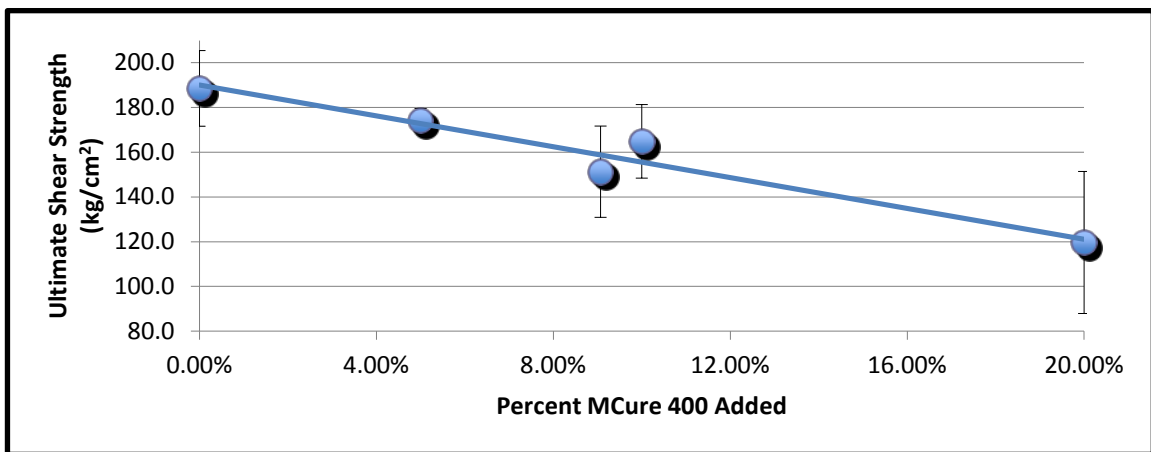


Figure 9. Averaged ultimate shear strength of DP-805 acrylate modified with 5.0%–20.0% with M Cure 400 (wet condition).

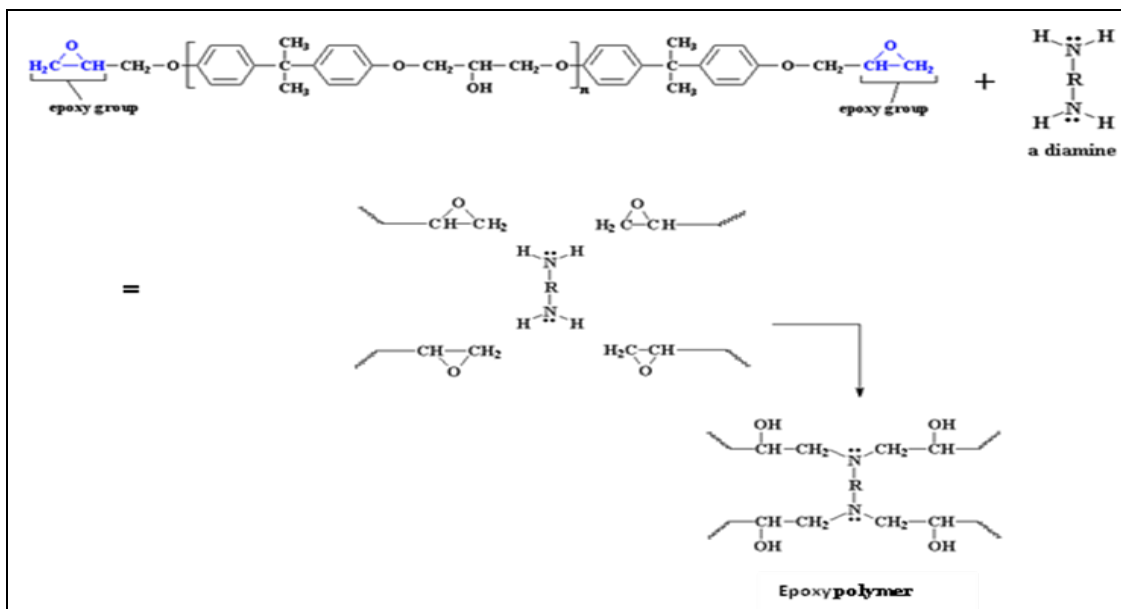


Figure 10. Polymerization of an epoxy resin with a diamine curing agent to form an epoxy polymer.

In the DP-805 system, which undergoes primarily a free-radical or anionic/cationic chain polymerization (figure 11), these reaction rates are dependent on the concentrations of initiators, catalysts and reactivity of the acrylate monomers leading to a less severe decrease in shear strength with the addition of M-Cure 400 monomer.

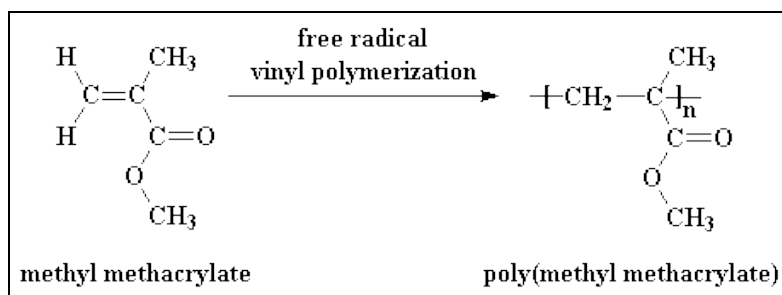


Figure 11. Free-radical polymerization of methyl methacrylate group to form poly) methyl methacrylate.

3.2 Time-Dependant Modified Shear Strength

The addition of M-Cure 400 improved rate at which the shear strength increased over time. Cure rates decreased when the additional weight-percent increase over 5% for both the 1-min epoxy and DP-805 (figures 12 and 13).

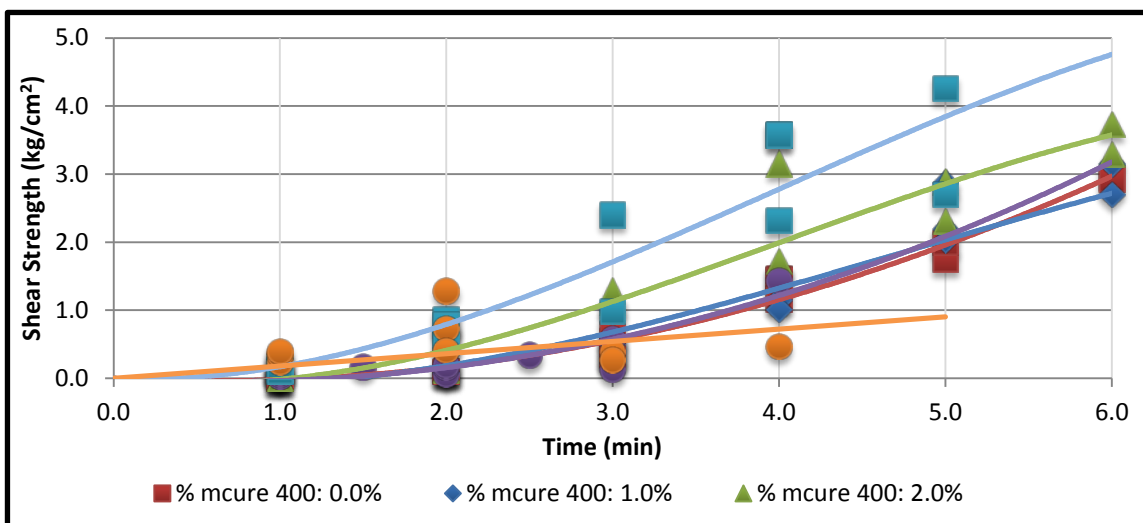


Figure 12. Max shear strength of 0.0%, 1.0%, 2.0%, 4.4%, 5.6%, and 7.0% modified with 1-min epoxy adhesives as cure time increases (wet condition).

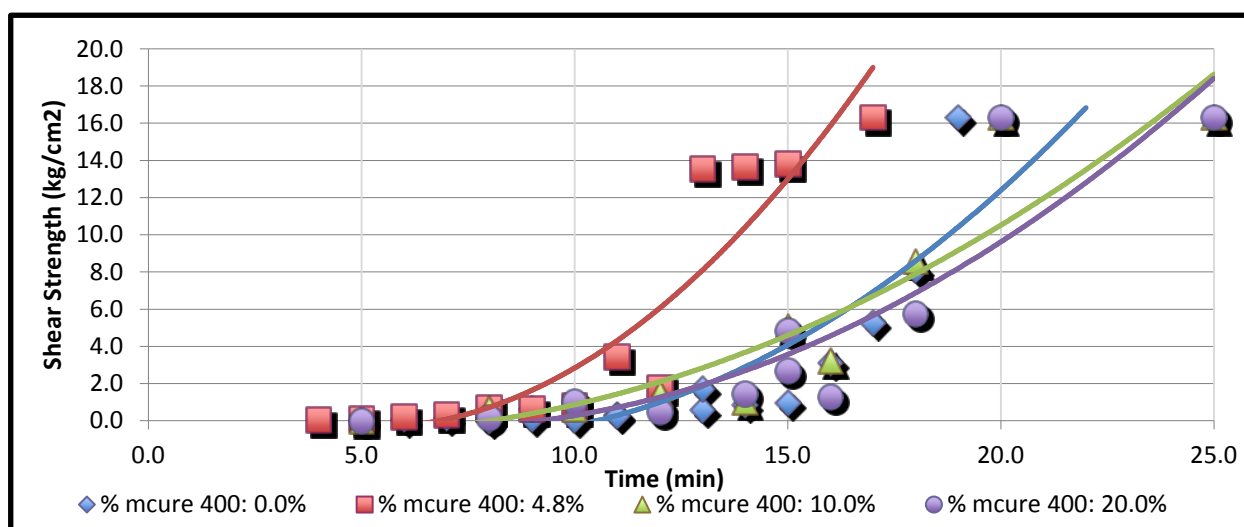


Figure 13. Max shear strength of 0.0%, 4.8%, 10.0%, and 20.0% modified DP-805 acrylate adhesives as cure time increases (wet condition).

3.3 Solvent Dispersion Effects

Solvents with ability to disperse water on a wet surface were of particular interest. Solvent dispersion effect was compared to that of the adhesive components and acrylate monomer additives. It was found that the DP-805 already had a fairly high dispersive ability of 38.1 mm (table 1). It was also found that some solvents like tetrahydrofuran and methyl ethyl ketone were strong polymer solvents and not practical for incorporation into adhesive formulations.

Table 1. Max radius of water dispersion by solvents.

Solvent	Max Radius Disperse (mm/in)
Dichloromethane	15.35/0.613
M Cure 400	15.8/0.625
Toluene	19/0.750
Benzene	31.75/1.125
3M DP-805 (monomer)	31.75/1.125
GPS (silane)	31.75/1.250
Methyl ethyl ketone	38.1/1.500
3M DP-805 (cure package)	38.1/1.500
Tetrahydrofuran	63.52/500
Nitromethane	38.1/1.5 (quick evaporation)
Chloroform	15.8/0.625 (near instant evaporation)

3.4 Addition of Solvents on Adhesive Performance

The various solvents were also tested to determine their effect on adhesive full gel (figure 14) and tack-free times (figure 15) in a 5-min epoxy system. The 5-min epoxy was chosen over the 1-min epoxy as it was initially thought a 1-min epoxy system would cure too quickly to detect differences performance. Solvents were not added to the acrylate system as its components already had high water dispersive properties. Results varied depending on the type and concentration of solvent added. Dichloromethane was determined to be too environmentally unfriendly for further formulation in a final product and were eventually dropped. Nitromethane and chloroform provided consistent improvements in gel and tack-free times. Tetrahydrofuran and carbontetrachloride provided consistent improvements in gel and tack-free times.

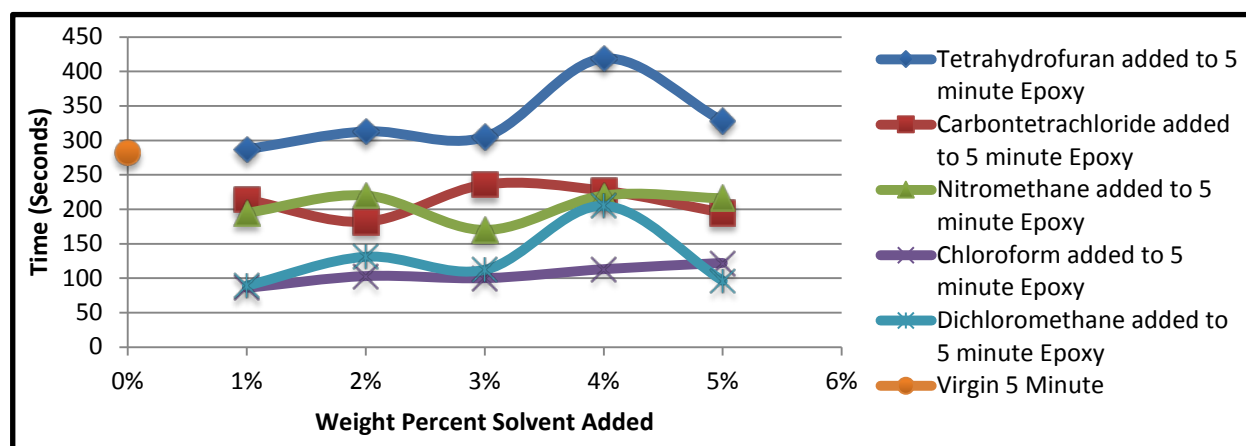


Figure 14. Fully gelled times for various solvent weight percents.

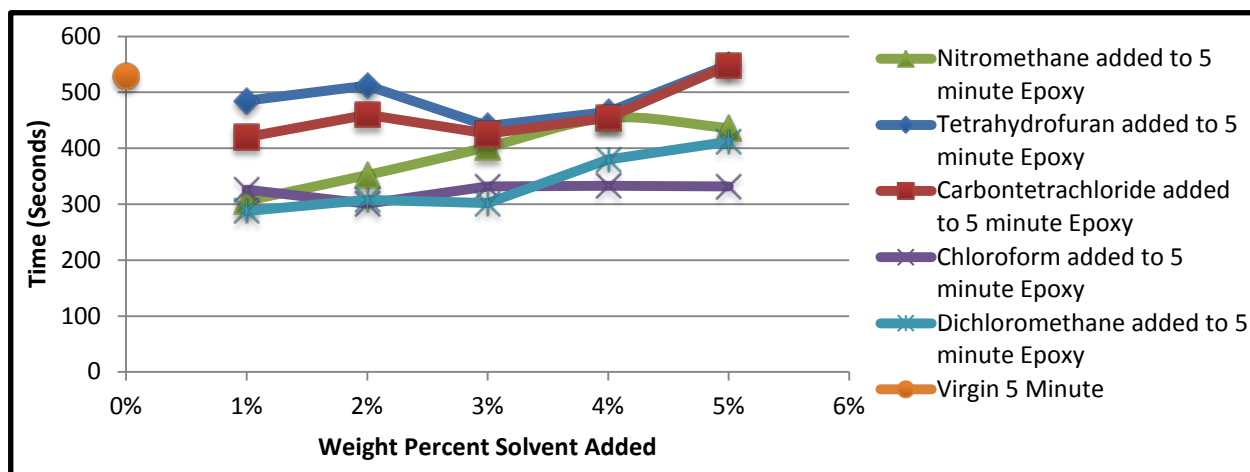


Figure 15. Tack-free/hard times for various solvent weight percents.

Nitromethane and chloroform were further tested in the 1-min system. The solvents were added to either the epoxy or cure side and tested. Testing later included 1-min epoxy modified with M-Cure 400. Figure 16 shows the optimal increase in immediate cure strength with a combination of 5 weight-percent M-Cure 400 with 1 weight-percent nitromethane added to the 1-min epoxy cure side. This was chosen to be the “finalized modified 1-min epoxy” for later testing. This increase is significant in the critical 0 to 4 min time range needed for a fast-curing adhesive. The unmodified 1-min epoxy has no bond strength at 2 min while the modified showed 2 kg/cm². At 5 min, the modified adhesive had more than double the bond strength of the unmodified epoxy.

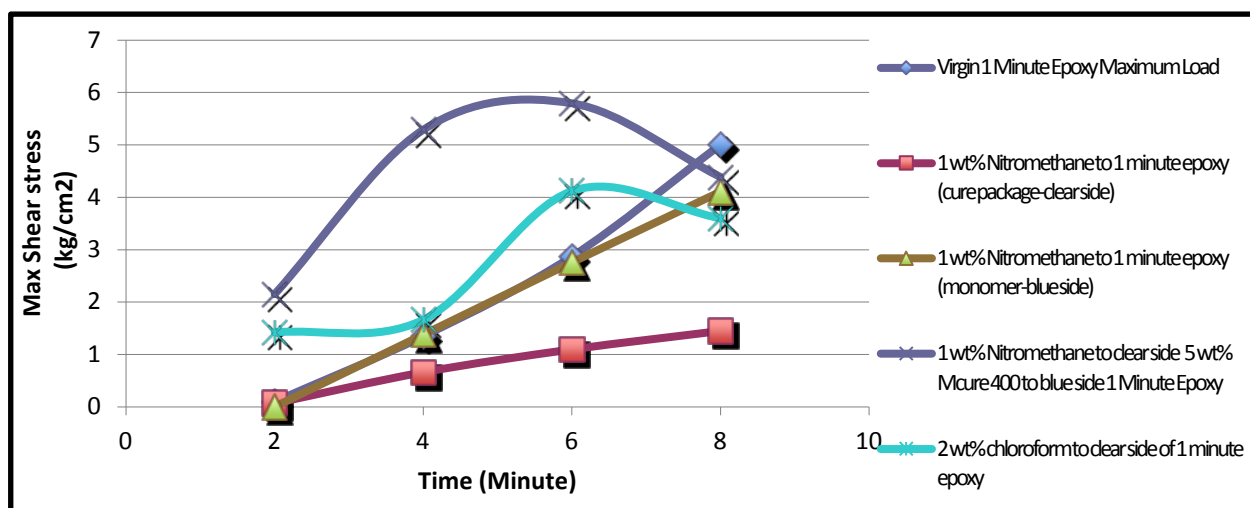


Figure 16. Comparison of chloroform and nitromethane with various formulations 1-min epoxy resin (wet conditions).

3.5 Water Uptake

Results indicated a fairly significant percent water uptake for the modified 1-min epoxy formulation, (figure 17). The absorption of water was less severe in saltwater than in the de-ionized water samples. When samples were cross sectioned, it appeared the majority of the water uptake was in the outer layer of the epoxy. The outer layer became white and noticeably softer than the remaining internal material. For this reason, application of the modified 1-min epoxy was done with thick bond lines and with as much surface coverage over the items being bonded as possible. This reduced water penetration into the service bond area.

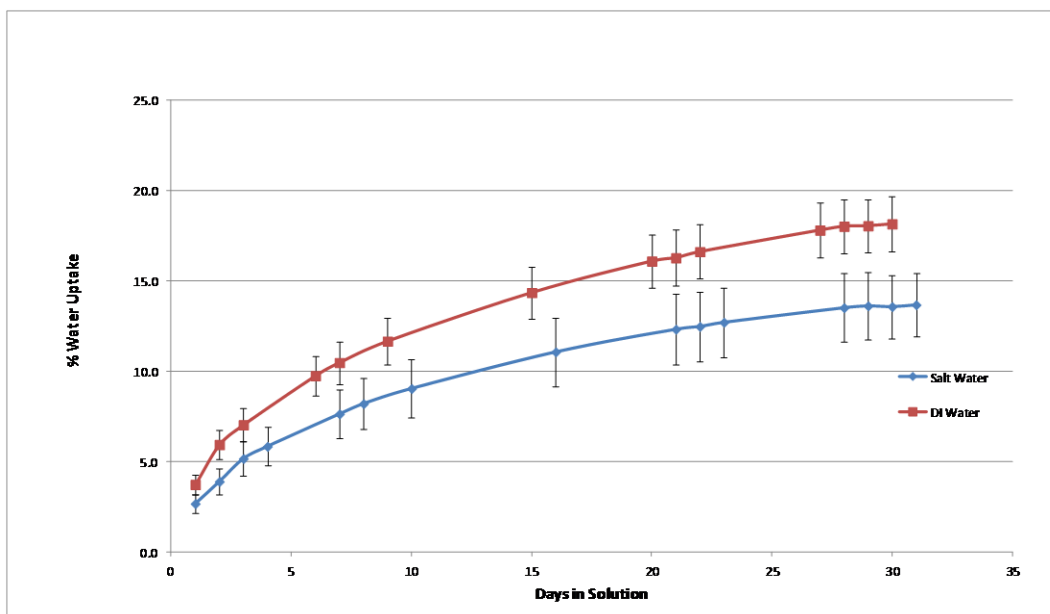


Figure 17. Water uptake for modified 1-min epoxy in de-ionized water and saltwater.

3.6 Viscosity

The rehometry results indicated that the modified DP-805 retained a fairly consistent viscosity and shear stress rates over the three month period (figures 18 and 19). A slight reduction was noted in both viscosity and shear stress after the first month but remained stable over the next two months. M Cure 400 added was significantly less viscous than pure DP-805 adhesive. The addition of 5 weight-percent to the monomer fraction of the adhesive did not cause any negative shelf-life issues.

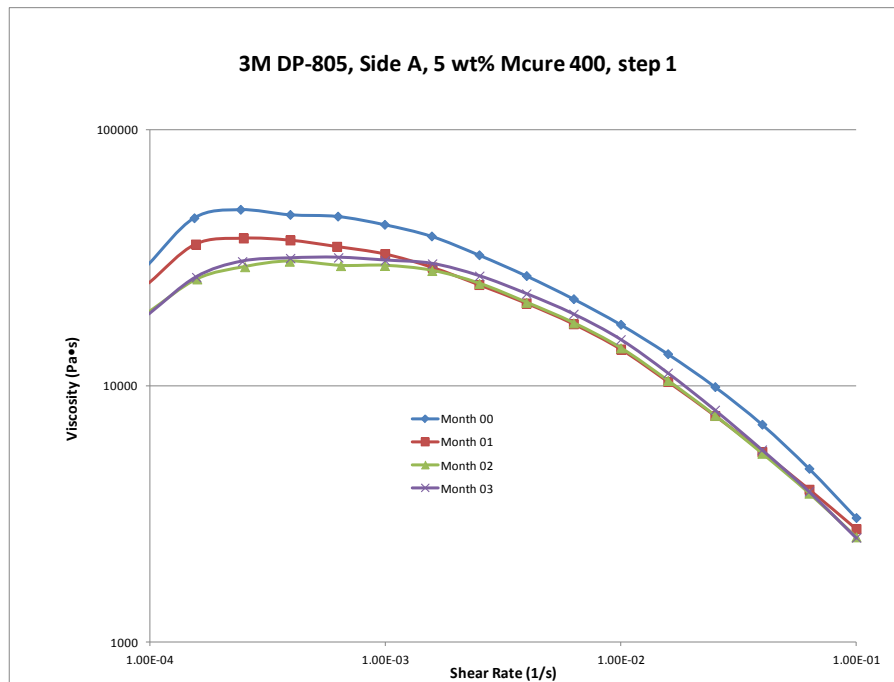


Figure 18. Viscosity change over 3 months in modified DP-805.

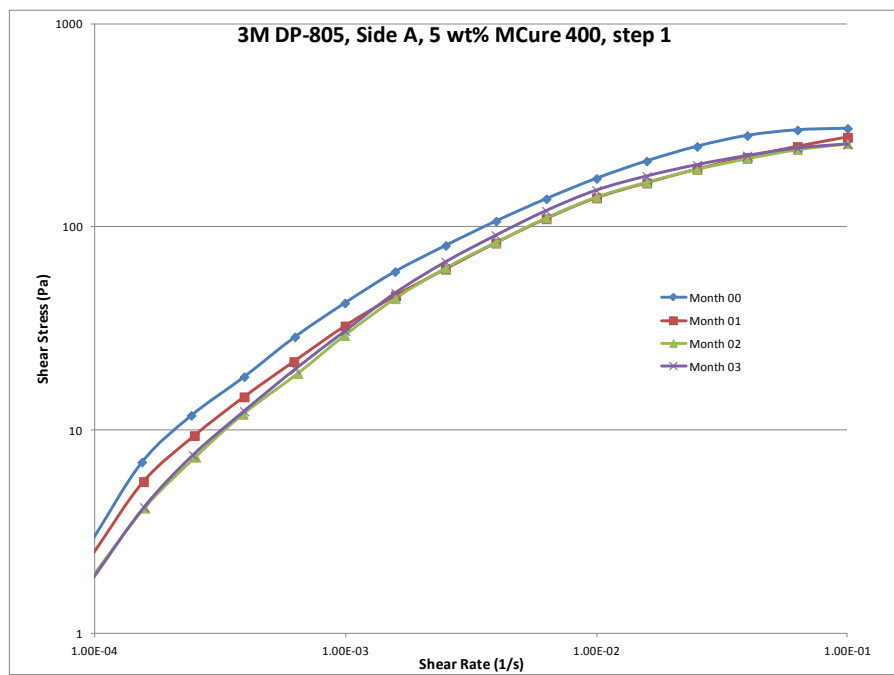


Figure 19. Shear stress change over 3 months in modified DP-805.

Modified components of the 1-min epoxy retained similar viscosity and shear rate properties compared to the baseline unmodified adhesive (figures 20 and 21). This was considered a success as many prior modifications to the epoxy had negative effects such as premature curing or clumping.

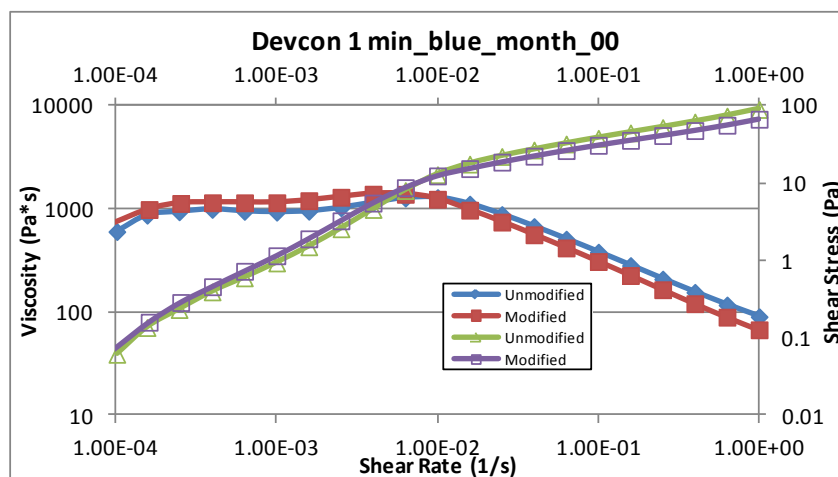


Figure 20. Initial viscosity and shear stress for modified and unmodified Devcon 1-min epoxy component.

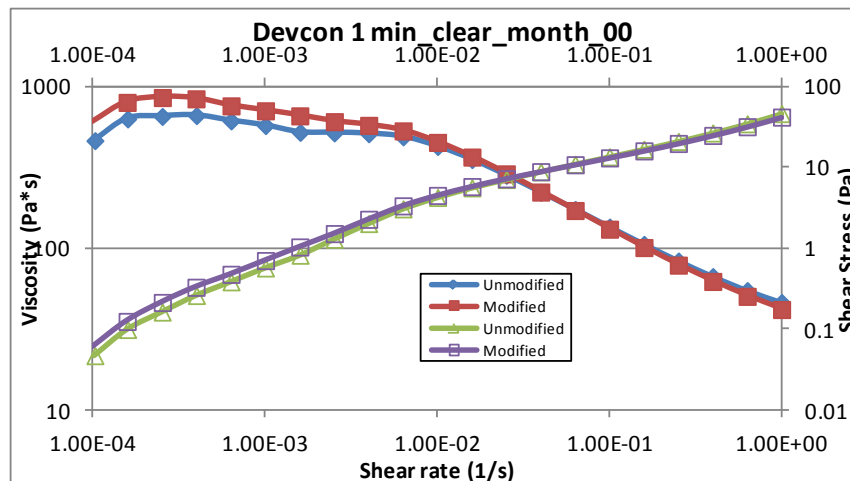


Figure 21. Initial viscosity and shear stress for modified and unmodified Devcon 1-min cure component.

After 3 months, the baseline 1-min epoxy showed signs of thickening. Its viscosity and shear rate increased noticeably over the baseline measurements. This was most significant in the epoxy fraction of the adhesive (figure 22). The modified and unmodified cure package side remained consistent to the baseline measurements.

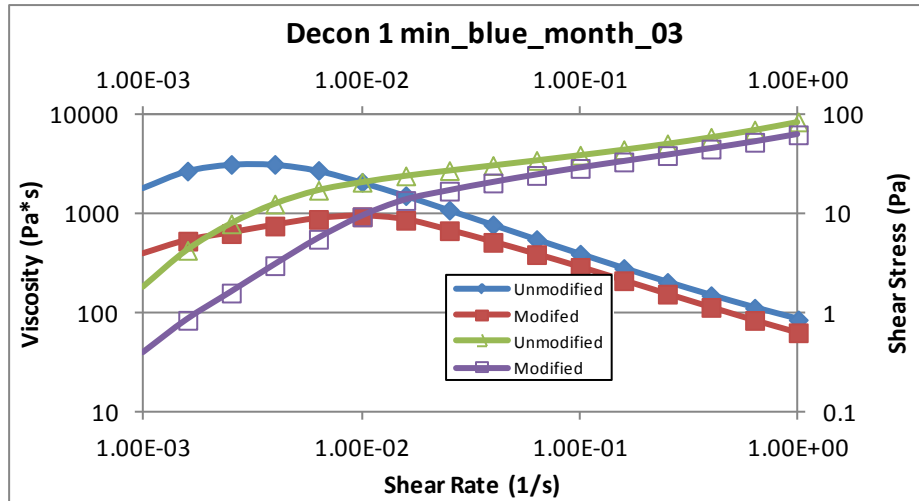


Figure 22. Three-month viscosity and shear stress for modified and unmodified Devcon 1-min epoxy component.

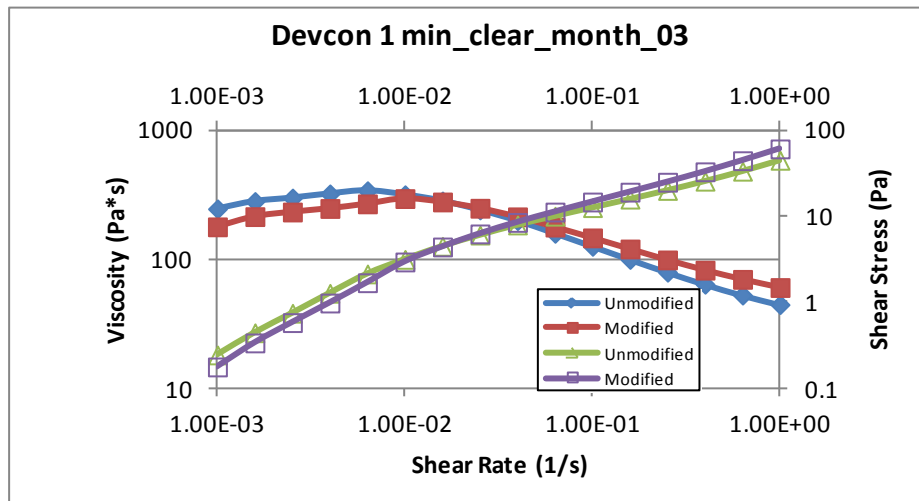


Figure 23. Three-month viscosity and shear stress for modified and unmodified Devcon 1-min cure component.

3.7 Application Method Testing

Adhesive applied underwater determined several useful techniques required for successful underwater application. Most important was the need to continue pumping the adhesive applicator gun. Once adhesive flowed through the mixing nozzle, any stoppage of flow would result in an immediate cure and blockage of the mixing nozzle. This was to be expected with such a fast-curing adhesive. Second, the thicker the adhesive bond layer the better. Additional uncured adhesive could be smeared at the bond edge to increase bond strength and decrease water penetration into the bond area. Working time was very short so operators often required

several practice attempts before being quick enough to apply and position the steel bonding object. With practice, the adhesive was easy to use underwater. Application testing results showed a fairly heavy metal object could easily be attached to an aluminum panel in a rapid manner (table 2).

Table 2. Application information for modified 1-min epoxy.

Temperature	0 °C 32 °F	20 °C 68 °F	30 °C 86 °F
Working time	15 s	5 s	3 s
Fixture time	5 min	2 min	1 min
Functional cure	50 min	30 min	20 min
Full cure	2.5 h	2 h	1.5 h

3.8 Representative Material Lap Shear Results

Lap shear specimens for materials marine relevant underwater bonding were tested in both saltwater and fresh water conditions for ultimate lap shear. Results showed very strong bonding was capable for the modified 1-min epoxy (figure 24). Samples were capable of achieving 105 kg/cm² (1500 psi) in lap shear tensile strength testing for both aluminum and composite substrates. Painted substrates failed due to delamination of the painted surface from the substrate. This limited the overall bond strength to that of the paint 70 kg/cm² (1000 psi). Samples exposed to 3.5 weight-percent salinity showed reduction in bond strength only with the aluminum samples. The aluminum showed definitive signs of corrosion including some in the edges of the bond area. This appeared to reduce the bond strength to that of 70kg/cm² (1000 psi). Composite samples aged in the saltwater bath showed no signs of being affected and retained similar bond strengths as those kept in tap water.

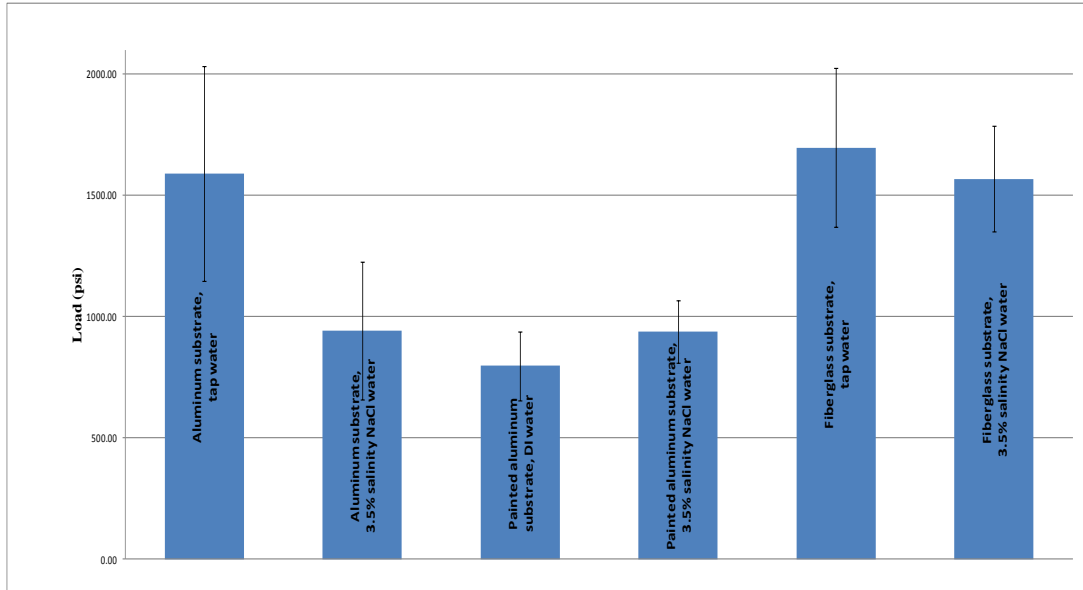


Figure 24. ASTM Standard D 3165-95-2 week full cure. Substrate failure occurred in painted samples; 3.5 weight-percent saltwater corroded aluminum substrate.

3.9 Finalized Material Bond Speed Comparison

Figure 25 shows the relative cure speeds for both the modified 1-min epoxy (adverse condition adhesive) along with the standard 1-min epoxy and the final modified DP-805 adhesive. As shown in the graph, the adverse condition adhesive was capable of achieving measurable bond strengths in as little time as 1 min.

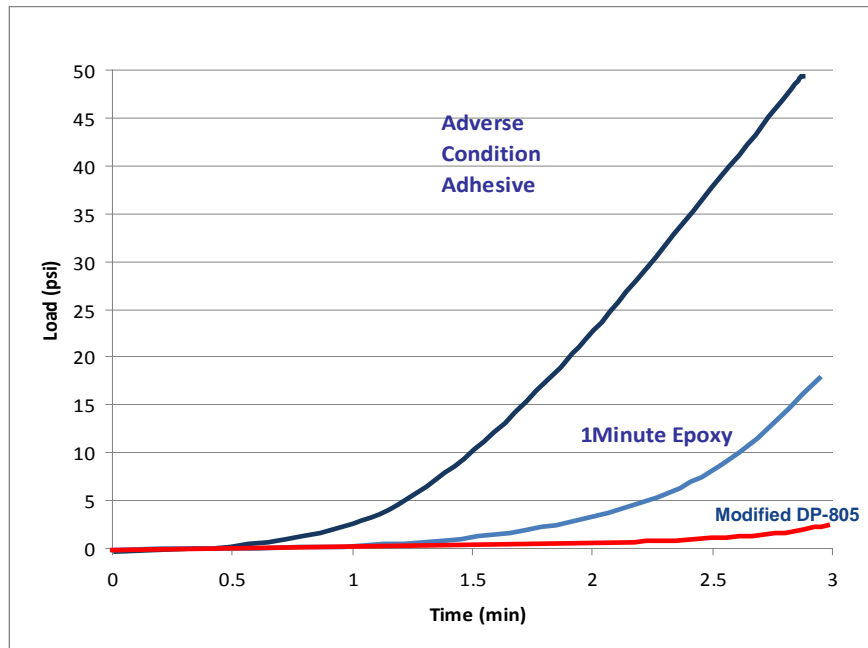


Figure 25. Comparison of underwater cure speed for 20 °C fresh water.

4. Conclusion

Formulating adhesives that cure well in aqueous environments has been difficult. This is due to water inhibiting good surface contact between the adhesive and substrate material, and the reduction in exothermic acceleration that most adhesives develop during cure (11, 12). ARL was able to formulate an epoxy adhesive that provided the desired fast cure speed even when applied and cured under water. This was accomplished by modifying a commercial 1-min epoxy. The epoxy was modified by the addition of a highly reactive acrylate monomer (Startomer M Cure 400) and a nitromethane solvent. The optimized formulation was a combination of 5 weight-percent M-Cure 400 added to the epoxy component and 1 weight-percent nitromethane added to the cure component side. As formulated the modified adhesive provided a faster cure speed than any available commercial adhesive. With such a fast cure speed, it was able to be applied and cure underwater. With practice, it was possible to consistently bond a 1/2-kg block of steel to an aluminum test panel underwater and obtain self sustaining bond in under 2 min at 20 °C. The epoxy demonstrated useful bond strengths even after two weeks in salt and fresh water conditions on a variety of substrates. ARL found that the modified 1-min epoxy did have a noticeable uptake of water over time.

For long-term underwater applications, ARL would recommend using a combination of the modified 1-min adhesive and the modified DP-805 (5 weight-percent M-cure 400 added to monomer component). The fast epoxy was optimal for quick bonding while the DP-805 provided longer term higher bond strength with faster curing compared to the unmodified DP-805. Overall, the speed in which the finalized modified epoxy cured underwater was very useful for the application it was designed. It rapidly bonded a variety of materials under water in under 2 min with enough bonding strength for the item to remain intact to fully cure in place. It is believed that this technology represents nearly the fastest practical two part adhesive underwater bond possible. Increasing the cure speed any faster would likely result in a poor application and less than optimal bonding. Ideally, the DP-805 could have been modified to cure as fast as the modified 1-min epoxy but retain its full-cure wet-cure strength. Unfortunately, all other attempts to modify the DP-805 for faster cure resulted in an unstable product with virtually no shelf life.

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